Dependence of the fundamental band gap of $Al_xGa_{1-x}N$ on alloy composition and pressure

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III-nitrides have been extensively studied in recently years because of their scientific and technological importance. In particular, the $Al_xGa_{1-x}N$ alloy system covers a wide ultraviolet (UV) spectral range between the direct band gaps of ~3.4 eV for GaN and ~6.2 eV for AlN at room temperature, and is very attractive for short-wavelength optical applications such as UV light emitters and UV detectors. In addition, AlGaN alloys with small mole fractions are used to form strained heterostructures with GaN and InGaN in light emitting diodes and laser diodes and in GaN/AlGaN field-effect transistors (FETs). Therefore, it is important to know the fundamental band gap of an $Al_xGa_{1-x}N$ epitaxial layer with a given mole fraction and its pressure dependence in order to calculate the band alignment for designing and engineering a device.

In this paper, we report an optical absorption study on $Al_xGa_{1-x}N$ epitaxial films with emphasis on the variation of the band-gap energy with alloy composition and the pressure dependence of the direct band gap of $Al_xGa_{1-x}N$ samples with different *x*. The bowing parameter which characterizes the nonlinear dependence of the fundamental band gap on the alloy composition was derived for the $Al_xGa_{1-x}N$ alloy system. The pressure coefficients of the direct Γ band gap were determined from the energy shift of the optical absorption edge with pressure for each individual sample.

The $Al_xGa_{1-x}N$ alloy samples were nominally undoped single-crystal epitaxial films grown by MOCVD on (0001) sapphire substrates. Thin AlN buffers were deposited on the substrates before the growth of the alloy films. The thickness of the $Al_xGa_{1-x}N$ epilayers varies from several thousand angstroms to over one micron. The AlN mole fractions of the samples were determined by Rutherford backscattering spectrometry. The experimental uncertainty for the determination of the *x* value is ±0.01. The light source for the optical absorption measurements was the bright continuous UV radiation from a bending magnet in the synchrotron at the Advanced Light Source of Lawrence Berkeley National Laboratory. A detection system consisting of a 0.5-m single-grating monochromator and a UV enhanced CCD detector was used for transmission measurements and for calibration of the light source. Pressure-dependent measurements were carried out using gasketed diamond anvil cells (DAC). All the absorption measurements were carried out at room temperature (295 K).

Figure 1 shows optical transmission spectra taken from several $Al_xGa_{1-x}N$ samples at atmospheric pressure. The band-gap energy is determined as the intersection of linear fits to the steeply declining transmission profile and the baseline above the transmission threshold. The inset of the figure plots the measured transition energies for the samples used in this work as a function of AlN mole fraction. The solid line is a least-square fit to our experimental data using

$$E(x)=E(0)+ax+bx^2, \qquad (1)$$

where $E(0)$=3.43 eV is the band-gap energy of GaN determined by the absorption measurements at room temperature, *x* is the AlN alloy fraction, and energy is given in eV. With the band-gap energy of AlN fixed at 6.2 eV,[4] the best fit using least-square fitting yields a=1.44 and b=1.33 eV. The obtained bowing parameter is larger than the value theoretically predicted by first-principle calculations (0.53 eV),[5] but is in good agreement with experimental values reported by Malikova *et al*.(0.98 eV)[6] and Agerer *et al*.(1.3 eV).[7]

Under applied pressure, the optical absorption edges shift towards higher energy as the direct band gaps of the alloy samples increase. The pressure-induced energy shifts for the optical transition related to the direct band gap are plotted in Fig. 2 for the $Al_xGa_{1-x}N$ samples with x=0.12, 0.2, 0.4, and 0.6. No pressure-dependent results obtained for the x=0.86 sample because its band-gap energy is larger than the transmission threshold of the diamond anvils (5.5 eV). The solid lines in Fig. 2 are least-square fits to the experimental data using a linear pressure-dependent fit function:

$$E(P)=E(0)+\alpha P, \qquad (2)$$

where the energy E is in eV and the pressure P is in PGa. The pressure coefficients yielded from the best fit to the experimental data are listed in Table I as "measured" α. These values do not exhibit a significant dependence on alloy composition. They are comparable to the pressure coefficients of excitonic transitions associated with the fundamental band gap of GaN[8-10] and are consistent with our previous photoluminescence results in $Al_xGa_{1-x}N$ alloys.[11]

Table I. Pressure coefficients for the fundamental band gap of $Al_xGa_{1-x}N$ epilayer samples

	$E(0)$ (eV)	$\alpha=dE/dP$ (meV/PGa) (Measured)	$\alpha=dE/dP$ (meV/PGa) (Corrected)
GaN	3.43	39.0[a];38.9[a,b]	41.4[a,b]
$Al_{0.12}Ga_{0.88}N$	3.64	37.3	40.4
$Al_{0.2}Ga_{0.8}N$	3.88	37.2	40.5
$Al_{0.4}Ga_{0.6}N$	4.22	37.6	41.2
$Al_{0.6}Ga_{0.4}N$	4.72	37.2	41.5

[a]Results were obtained by photoluminescence measurements.
[b]Ref. 20.

It is known that nitride epitaxial films grown on sapphire substrates are always subjected to slight compression primarily caused by the difference between the thermal-expansion coefficients of the epilayers and the substrates. Application of hydrostatic pressure to such a strained system consisting of materials with different bulk moduli will lead to uniaxial strains that make the epilayer and the substrate experience different effective hydrostatic and axial pressure components.[12,13] Since the bulk modulus of sapphire (~240 GPa)[14] is larger than that of GaN (~210-237 GPa)[15-17] and AlN (218 GPa),[18] the deformation of nitride epilayers deposited on sapphire is affected by the compression of the stiffer substrates under hydrostatic pressure. Under hydrostatic pressure conditions, a tensile strain will be induced in the compressively strained $Al_xGa_{1-x}N$ epilayers to compensate the applied hydrostatic pressure because $Al_xGa_{1-x}N$ has a larger compressibility. As a result, the $Al_xGa_{1-x}N$ layers effectively experience a smaller hydrostatic pressure and an additional (0001) uniaxial stress.

In order to derive the actual pressure coefficients for the AlGaN samples from the measured values, one has to estimate the effective pressure experienced by AlGaN epilayers. The sample volume change with applied pressure can be described using the Murnaghan equation of state:[19]

$$V(P)=V(0)[1+(B'/B)P]^{1/B'}, \qquad (3)$$

where B is the bulk modulus and B' is its pressure derivative ($=dB/dP$). For a crystal with wurtzite structure, the relative volume change can be related to the variation of lattice parameters a and c as $\Delta V/V=2\Delta a/a+\Delta c/c$. The relative changes of the lattice parameters are related through the elastic stiffness coefficients as $\Delta c/c=-2(C_{13}/C_{33})\Delta a/a$. Using a first-order (linear) approximation, Eq.(3) can be further reduced to

$$a(P)/a(0) = P/[2B\,(1- C_{13}/C_{33})] \qquad (4)$$

Figure 3 plots out the calculated $a(P)/a(0)$ for GaN and AlN as a function of applied hydrostatic pressure using Eq.(4) under two extreme conditions: (1) unstrained (free-standing) $Al_xGa_{1-x}N$ epilayers with their deformation under pressure independent of the volume change of

sapphire, and (2) “pseudomorphically” strained epilayers with their in-plane compressibility completely determined by the compression of sapphire at high pressures. An averaged value of B=223.5 GPa from Refs.15-17 was used for GaN in the calculation. The overall effect of mechanical strain is to make a strained layer on a stiffer substrate be compressed less than a free-standing layer at a given externally applied hydrostatic pressure. The effective hydrostatic pressure experienced by the assumed “pseudomorphically” strained $Al_xGa_{1-x}N$ epilayers is smaller than applied pressure. The stress reduction ranges from ~8-12% depending on the alloy composition. The pressure coefficients for the $Al_xGa_{1-x}N$ samples derived from the mechanical correction to the experimental measured values are listed in Table I as “corrected” values.

It has to be pointed out that the “pseudomorphically” strained condition should be relaxed in reality. Perlin *et al.* recently found a 6% reduction of the experimentally measured pressure coefficient for GaN on sapphire (strained) as compared to that for free-standing GaN (unstrained),[20] which is smaller than an 8% predicted in Fig. 3 for GaN. One of the possible reasons leading to a smaller effect of stress reduction is that the highly defective AlN buffers are most likely to be, at least partially, plastically deformed under applied pressure. Therefore, we regard the corrected values for the pressure coefficients listed in Table I as the upper limit for the pressure dependence of the fundamental band gaps of the $Al_xGa_{1-x}N$ alloy samples.

In conclusion, optical absorption measurements were performed to study the fundamental band gap of $Al_xGa_{1-x}N$ as a function of alloy composition and applied pressure. The $Al_xGa_{1-x}N$ samples were found to exhibit a large nonlinear variation of the fundamental band gap with a bowing parameter of 1.33 eV. The fundamental band gaps of the $Al_xGa_{1-x}N$ samples were found to linearly increase under applied pressure. We derived the pressure coefficients for the direct band gap of $Al_xGa_{1-x}N$ to be around 40-41 meV/PGa from the experimentally measured values by taking into account the difference of compressibility between the epitaxial films and sapphire substrate.

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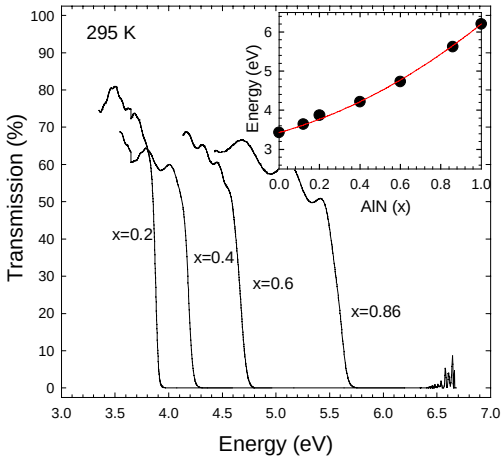

Figure 1. Transmission spectra taken from several $Al_xGa_{1-x}N$ epitaxial layers at atmospheric pressure. The inset plots the measured band-gap energies as a function of AlN mole fraction. The solid line is the best fit to the experimental data.

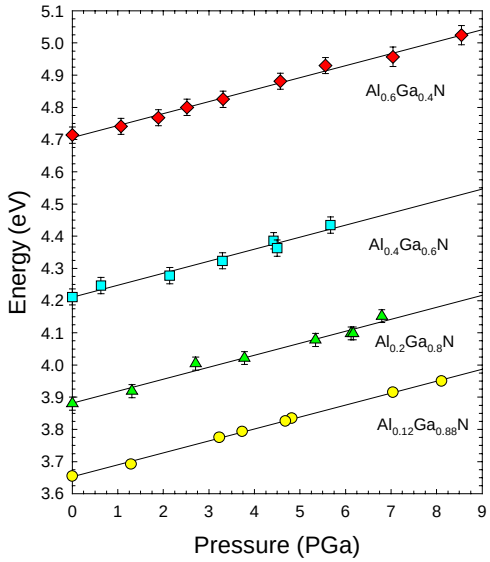

Figure 2. The energy positions of the optical transitions associated with the direct band gaps of $Al_xGa_{1-x}N$ samples as a function of applied pressure.

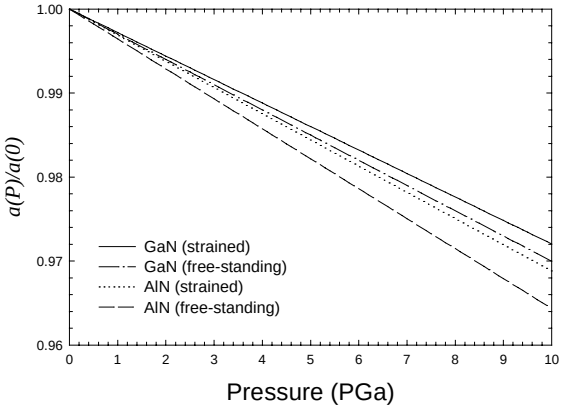

Figure 3. Calculated change of in-plane lattice constant *a* of GaN and AlN with pressure under free-standing and "pseudomorphically" strained conditions using linear elastic approximation. The pressure-induced volume change for free-standing $Al_xGa_{1-x}N$ lies in between the lines of GaN and AlN.